Magnetic-Field-Driven Superconductor-Insulator-Type Transition in Graphite

H. Kempa [a], Y. Kopelevich [a,1], F. Mrowka [a], A. Setzer [a],
J. H. S. Torres [a,1], R. Höhne [a] and P. Esquinazi [a]

[a]*Department of Superconductivity and Magnetism, Institut für Experimentelle Physik II, Universität Leipzig, Linnéstr. 5, D-04103 Leipzig, Germany*

Abstract

A magnetic-field-driven transition from metallic- to semiconducting-type behavior in the basal-plane resistance takes place in highly oriented pyrolytic graphite at a field $H_c \sim 1$ kOe applied along the hexagonal c-axis. The analysis of the data reveals a striking similarity between this transition and that measured in thin-film superconductors and Si MOSFET's. However, in contrast to those materials, the transition in graphite is observable at almost two orders of magnitude higher temperatures.

Key words: A. metals, semiconductors D. phase transitions

The anomalous carrier density, temperature, magnetic and electric field dependence of the resistivity observed in various two-dimensional (2D) electron and hole systems [1] as well as in superconducting thin films [2,3] remains still without an accepted explanation. Transport measurements in Si MOS-FET's with large enough carrier density reveal that the resistivity drops by a large factor as the temperature decreases below a temperature $T \sim \frac{1}{3}T_F$ (T_F is the Fermi temperature) indicative of a clear metallic behavior. Taking into account the observed magnetic field suppression of the metallic behavior [1], the possible existence of a superconducting phase in two dimensions in Si MOSFET's has been suggested [4] based mainly on the field-induced superconductor-insulator (SI) transition scaling analysis [5].

Recent studies of highly oriented pyrolitic graphite (HOPG) suggest the occurrence of high-temperature superconducting correlations in this material [6,7].

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[1] On leave from Instituto de Fisica, Unicamp, 13083-970 Campinas, Sao Paulo, Brasil.

Noting that graphite is a quasi-2D semimetal with a low carrier density (electrons and holes) so that Coulomb interaction effects can be important (the concentration of the majority carriers is $\sim 2 \times 10^{18}$ cm^{-3} and of the minority carriers is $\sim 6 \times 10^{16}$ cm^{-3} [8–11]) it seems reasonable to ask whether some of the ideas regarding superconductivity in MOSFET's [1,4,12–14] may be also applicable to graphite.

In this work we have studied both magnetoresistance and magnetization of HOPG samples with the basal plane resistivity ρ ranging from $\rho(T = 300 \text{ K}) =$ 5 $\mu\Omega$cm to 135$\mu\Omega$cm. Our results demonstrate that a field $H = H_c \sim 1$ kOe applied parallel to the hexagonal c-axis, induces a transition from metallic-($\mathrm{d}R/\mathrm{d}T > 0$, R is the measured resistance) to semiconducting-type ($\mathrm{d}R/\mathrm{d}T <$ 0) behavior. The analysis of the transport data, in particular the obtained scaling reveals a striking similarity to that measured in 2D superconductors [2,3,15–17] and Si MOSFET's [1,4]. Here we concentrate mainly on the data obtained for the sample with the lowest resistivity (sample HOPG-3).

HOPG samples were synthesized at temperatures $T \sim 2700 \ldots 3000$ ^{o}C and pressure $P \sim 10 \ldots 30$ MPa at the Research Institute "Graphite" (Moscow) and characterized by means of x-ray diffraction (the analysis of the rocking curves FWHM indicate for the different samples: HOPG-1: 1.4^o, HOPG-2: 1.2^o, HOPG-3: 0.5^o), SEM, STM, and spectrographic analysis techniques [6,7]. Dc magnetization $M(H,T)$ measurements were performed with the SQUID magnetometer MPMS7 (Quantum Design). The dc resistance $R(H,T)$ was measured in the temperature interval 2 K - 300 K in applied magnetic field $0 \leq H \leq 9$ T using a standard 4-probe method with both current and voltage leads patterned on the sample surface. Resistivity values were obtained with a lead geometry that assures an uniformly distributed current over the sample cross section. The amplitude of the applied current was between 10 μA and 1 mA at which no Joule heating was detected. In all transport measurements the current was inverted in order to eliminate thermoelectric effects.

Figure 1 shows the normalized resistance $R(T)/R(300 \text{ K})$ measured for samples with $\rho(300 \text{ K}) = 45\mu\Omega$cm (sample HOPG-1), $\rho(300 \text{ K}) = 135$ $\mu\Omega$cm (sample HOPG-2), and $\rho(300 \text{ K}) = 5$ $\mu\Omega$cm (sample HOPG-3). As can be seen from Fig. 1, at $T > 200$ K all three samples show a semiconducting-type temperature dependence. At lower temperatures $R(T)$ obtained for the less resistive samples (HOPG-3 and HOPG-1) crosses over to a metallic behavior ($\mathrm{d}R/\mathrm{d}T > 0$) below $T \sim 200$ K and $T \sim 50$ K, respectively. However, in the sample HOPG-2 with the highest resistivity, $\mathrm{d}R/\mathrm{d}T < 0$ down to $T \sim 30$ K below which $R(T)$ saturates. We stress that the $R(T)$-curves shown in Fig. 1 are not specific to our samples: both metallic- and nonmetallic-type $R(T)$ generally occur in HOPG depending on the heat treatment [8,9]. Figure 1 also illustrates that a weak (~ 1 kOe) magnetic field $H||$c-axis suppresses the metallic-type state in the HOPG-1 sample.
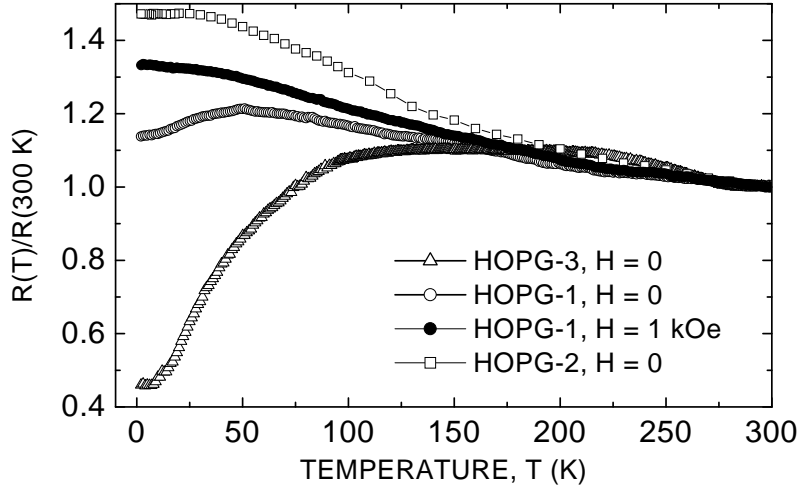
Fig. 1. Temperature dependence of the reduced basal-plane resistance $R(T)$ obtained for three graphite samples (HOPG-1, -2, and -3) in zero applied magnetic field and also in $H = 1$ kOe for HOPG-1 sample.

A pronounced magnetic-field-induced transition from metallic- to semiconducting-type $R(T)$ is observed in sample HOPG-3, as shown in Fig. 2(a). The $R(T)$ data plotted in Fig. 2(a) for various applied magnetic fields were obtained from isothermal magnetoresistance $R(H)$ measurements. Figure 3 shows several $R(H)$ isotherms in the vicinity of the "crossover" field $H_c = 1140$ Oe at which the $R(H)$ data obtained at temperatures 50 K, 100 K and 200 K intersect.

Noting that the results of Fig. 2(a) resemble very much the resistance behavior in the vicinity of the magnetic-field-driven metal-insulator (MI) [1,4] and SI [2,3,15–17] transitions we apply here the same scaling approach [2–5,15,17] to the transition measured in HOPG. According to the scaling analysis, the resistance in the critical regime of the quantum SI transition is given by $R(\delta, T) = R_c f(|\delta|/T^{1/z\nu})$, where R_c is the resistance at the transition, $f(|\delta|/T^{1/z\nu})$ the scaling function such that $f(0) = 1$, z and ν are critical exponents, and δ is the deviation of a variable parameter from its critical value. With $\delta = H - H_c$, we have plotted in Fig. 2(b) R vs. $|\delta|/T^{1/\alpha}$, where $\alpha = 0.65 \pm 0.05$ was obtained from the log-log plot of $(\mathrm{d}R/\mathrm{d}H)|_{H_c}$ vs. T^{-1}. The collapse of the resistance data into two distinct branches, below and above the critical field H_c, is obtained in the temperature range 50 K - 200 K, see Fig. 2(b). At $T < 20$ K, where the resistance saturation is apparent, see Fig. 2(a), a clear deviation from the scaling is evident, reminiscent of the behavior observed in amorphous Mo-Ge films [17] where still unknown dissipation effects [17,18] lead to the saturation of the resistance at low temperatures. Interestingly, the obtained value of the exponent $\alpha = 0.65 \pm 0.05$ for HOPG
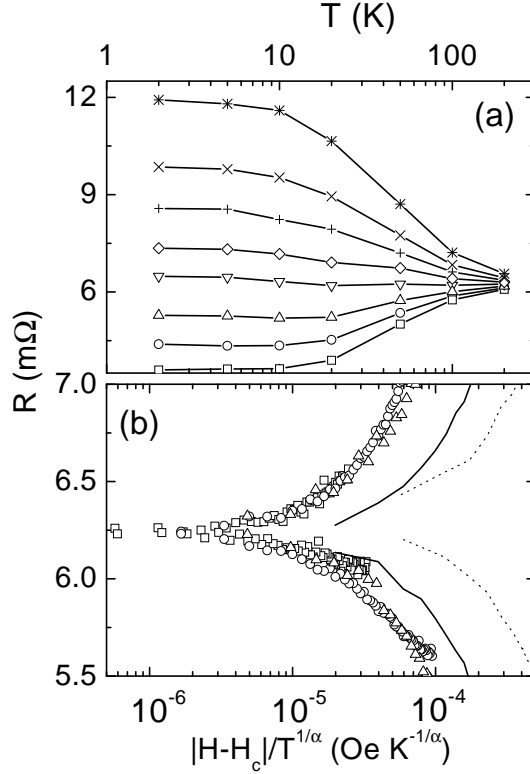
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Fig. 2. (a) $R(T)$ obtained for HOPG-3 for selected magnetic fields using magnetoresistance data: ($\square$)$H = 500$ Oe, ($\circ$)700 Oe, ($\triangle$)900 Oe, ($\triangledown$)1140 Oe, ($\diamond$)1300 Oe, (+)1500 Oe, ($\times$)1700 Oe, ($*$)2000 Oe. (b) Resistance measured at $T = 200\text{K}(\square), 100\text{K}(\circ), 50\text{K}(\triangle), 20\text{K}(-)$, and 10K (- -) as a function of the scaling variable where $H_c = 1140$ Oe and $\alpha = 0.65 \pm 0.05$.

coincides with that found in the scaling analysis of both the magnetic-field-tuned MI-type transition in Si MOSFETS's ($\alpha = 0.6 \pm 0.1$ [4]) and the SI transition in ultrathin a-Bi films ($\alpha = 0.7 \pm 0.2$ [3]).

We would like to stress the similarities in the transport properties of HOPG and those of a 2D electron gas as in Si MOSFET's: (1) The occurrence of metallic or semiconducting behavior in graphite at $H = 0$ (see Fig. 1) is very sensitive to the carrier density which can be changed by, e.g., annealing [9]. (2) The characteristic temperature T^* (~ 100 K for sample HOPG-3) below which $\rho(T)$ strongly decreases is a considerable fraction of the Fermi temperature $T_F \sim 250$ K [11]. (3) There is a clear suppression of the conducting phase by a magnetic field. (4) There exists a critical scaling with a remarkably similar exponent α.

There is, however, an important difference between the results in HOPG and those obtained in Si MOSFET's. Whereas the magnetoresistance in Si MOSFET's is independent of the direction of the applied magnetic field [1],
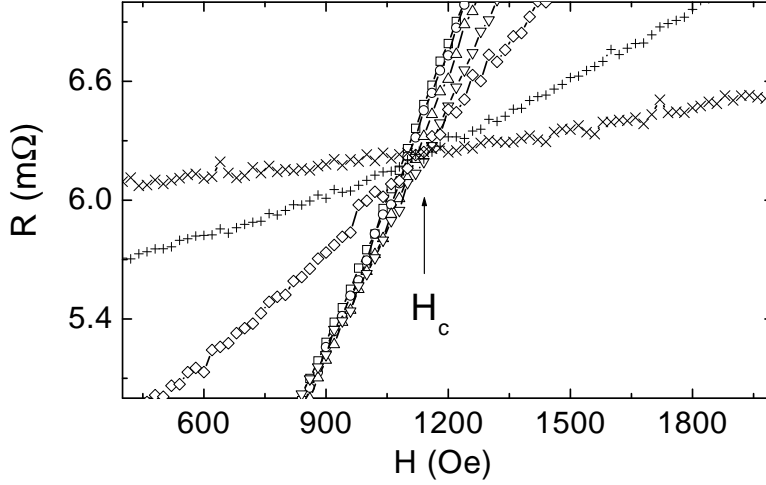
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Fig. 3. Magnetoresistance $R(H)$ isotherms measured in HOPG-3: ($\square$) $T = 2$ K, ($\circ$)5 K, ($\triangle$)10 K, ($\triangledown$)20 K, ($\diamond$)50 K, (+)100 K, ($\times$)200 K. $H_c = 1140$ Oe is the "crossover" field.

$\Delta R/R$ measured in HOPG is two orders of magnitude larger for $H||$ c-axis as compared to the perpendicular orientation. In other words, while a spin-polarization mechanism seems responsible for the transition in Si MOSFET's, orbital effects are dominant and influence the transition in HOPG.

We note that the scaling shown in Fig. 2(b) can be related to the field-tuned quantum transition if the critical regime extends to $T \sim 200$ K, at least. Although this may appear unlikely, the special characteristic of graphite must be taken into account: Because of the low density and extremely small effective masses of the carriers in graphite, as well as its quasi two-dimensional nature, one expects a strong enhancement of quantum effects. Figure 4 shows the experimental evidence for quantum oscillations due to de Haas-van Alphen (DHVA) effect at $T = 5$ K (a), 100 K (b) and 300 K (c). The occurrence of DHVA oscillations at low fields arising from the minority carriers was already reported in the literature [8–10]. It is interesting to note, however, that these oscillations become particularly clear at $H \geq H_c \sim 1$ kOe where the SI-type transition takes place, see Fig. 2.

The following points should be considered regarding the origin of possible superconducting correlations in HOPG. (a) We would like to emphasize the potential importance of the minority carriers in HOPG. The effective mass of the minority carriers $m^* \sim 0.004m_0$ is 10 to 15 times smaller than the effective mass of the majority holes ($m^* \sim 0.04m_0$) and electrons ($m^* \sim 0.06m_0$) [8–11] (m_0 is the free-electron mass). This may lead to superconducting instabilities in the electron-hole liquid as discussed in Refs.[19–21]. (b) On the other hand,
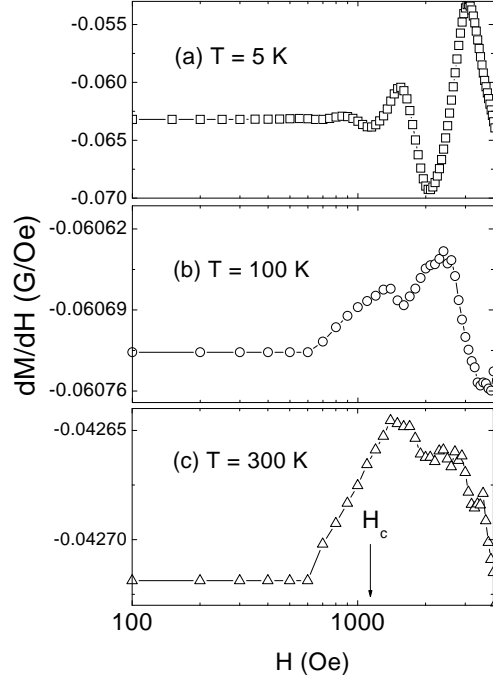
Fig. 4. Field derivative of the measured magnetization (without any subtraction) as a function of applied field for sample HOPG-3 at three temperatures.

the coexistence and interplay of superconducting and ferromagnetic states [6,22] may indicate the relevance of p-wave pairing mediated by ferromagnetic spin fluctuations [14,23].

To conclude, the present work provides evidence that at least some of the physical concepts proposed to describe the magnetic-field-tuned SI-type transition in various 2D systems should also be applicable to graphite. The "reentrant" metallic-type behavior observed in the regime of lowest Landau level quantization for both HOPG [7] and Si MOSFET's [24] further suggests a deep similarity of the physical processes operating in these systems.

Acknowledgements

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